ENVIRONMENTAL EMISSIONS MANAGEMENT AT THE LA CARIDAD COPPER SMELTER

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ABSTRACT

The La Caridad copper smelter, located in Nacozari, Mexico, have started a multi-year plan to reduce sulphur dioxide and particulate matter emissions into the environment. In 2014 the smelter completed a voluntary plant-wide SO₂ process emissions inventory as part of the smelter's proactive environmental stewardship policy. In turn, this triggered the development of several environmental projects to alleviate these emissions. A strategy consisting of improved capture efficiency of the sources with greatest impact has been followed to maximize cost-effectiveness. The reduction of secondary emissions from the Teniente Converter, as well as of primary and secondary emissions from the Peirce-Smith Converters have been key areas of priority. Additionally, a new system to capture and recover particulate matter from the Anode Refining Furnaces off-gas is also in the process of being implemented. This paper presents an overview of the work developed behind this effort and the smelter's vision towards a greener future.

KEYWORDS

Copper smelter, Emission abatement, Sulfur dioxide, Particulate matter

INTRODUCTION

The La Caridad copper smelter is owned and operated by Metalurgica de Cobre S.A. de C.V. (a subsidiary of Grupo Mexico). Currently, the smelter has a production capacity of 300,000 tonnes of anodic copper per year. The smelter is coupled with a 300,000 t/y electrolytic refinery. Other by-products (such as precious metals and sulfuric acid) are also generated as part of an integrated process. The original smelter started operating in 1986 with one Furukawa concentrate dryer, one Outokumpu Flash Smelting Furnace (FSF), two slag cleaning electric furnaces (SCFs), three Peirce-Smith Converters (PSCs), two Anode Refining Furnaces (ARFs) and one casting wheel. In 1997, a plant expansion project was concluded with the installation of one steam dryer, one Modified Teniente Converter (MTC), one additional ARF, one additional casting wheel, and the electrolytic refinery [1].

Over the years, the smelter management has implemented numerous environmental projects to alleviate SO₂ and particulate matter (PM) emissions. The smelter process gas handling system captures the process gases from the FSF, MTC, and the three PSCs. The process gases are cleaned and conditioned and sent to the two acid plants. The first acid plant (with a capacity of 226,000 Nm³/h, wet basis) was commissioned in 1988 to process the FSF and PSC off-gases. A second acid plant (with a capacity of 195,000 Nm³/h, wet basis) was commissioned as part of the smelter expansion project [1]. The PSCs also have a secondary gas handling system with a dedicated baghouse and stack. The Furukawa dryer off-gas reports to a dedicated electrostatic precipitator (ESP) for dedusting before venting via a local stack. Process gas from the two SCFs, along with hygiene ventilation from various sources inside the smelter (including matte and slag tapping hoods from the FSF) report to a baghouse-based gas handling system and vent to atmosphere via a local stack. The original ARFs do not have an off-gas handling system, however, each ARF has a post-combustion chamber which naturally vents the process gases to the atmosphere via a dedicated stack.

From 2008 to 2010, an improvement project was undertaken to replace the PSCs primary hoods and to modify the corresponding gas handling system. The original radiative cooling chambers and common ductwork header (upstream to the ESPs) were eliminated, implementing instead a gas quencher with a single

ductwork leading to a dedicated ESP. Additionally, the original secondary hoods were replaced with a new design.

VISION FOR A GREENER FUTURE

Grupo Mexico's focus is the Sensible Development of its business, and that's why a sustainability strategy has been defined based on three pillars that guide all operating units' performance: to grow and share value, to foster wellbeing and security, and to care for, preserve and renew the environment.

The Metalurgica de Cobre operation is aligned with the industry's best practices, always searching to minimize the environmental impact and to preserve the environment on which all activities take place. Six lines of action have been defined as part of the environmental management system:

- Rational use of water and natural resources
- Emissions reduction
- Efficient energy usage
- Biodiversity preservation
- Reforestation
- Comprehensive waste management

In relation to the second line of action, in 2014, the La Caridad smelter management commissioned Gas Cleaning Technologies LLC (GCT) to undertake a smelter-wide SO₂ emissions reduction evaluation. This evaluation resulted in a series of recommended improvement projects that were prioritized (highest-impact and lowest capital expenditure projects with highest priority) into a long-term improvements master plan. This paper summarizes the work completed to generate the master plan and the improvements accomplished to date.

EVALUATION APPROACH

The evaluation relied on the generation of an SO_2 inventory as a data baseline foundation. Measurements were made to quantify the SO_2 fugitive emission rates from the roofline above the various process vessels and hot metal transfer operations as well as SO_2 stack emissions from the ARF stacks, the steam dryer stack, the Furukawa dryer stack, and the SCF and hygiene stack.

GCT's approach consists, in essence, in quantifying the building's SO_2 fugitive emissions and correlating these to the discrete primary (e.g., blowing) and secondary (e.g., tapping) process activities at the FSF, PSCs, and ARFs. This, in turn, allows to generate a ranking matrix with the various sources from highest to lowest daily average emission rate.

The building roofline measurements were performed using several manifolds to measure flow rate, temperature, and SO_2 concentrations. Roofline measurements provide more reliable emission measurements as sampling is easier to maintain at this location and the opening area for volumetric flow measurement is well defined. Continuous SO_2 measurements were made using a manifold at the monovent above the FSF and each operating PSC, ARF, and SCF. For each testing case, multiple sampling trains were utilized simultaneously.

During the testing period, GCT performed ventilation surveys to measure air flow rates and temperature in and out of the various major openings across the smelter buildings. These surveys were used to define the building ventilation rates and to determine fume flow patterns through the buildings.

In addition to the roofline measurements and ventilation surveys, portable gas analyzers were used to measure SO_2 concentrations locally at various locations inside the buildings. This represented an additional dataset useful to further validate the roofline emissions measurements and provide a relative indication of fugitive emissions from other locations not being tested by the roofline sampling trains. Flow rate and SO_2 emissions measurements were also undertaken at individual stacks.

This evaluation approach has been successfully applied by GCT at several copper smelters and steel melt shops internationally.

Only SO_2 roofline emissions were measured, while roofline PM emissions were estimated for indicative guideline purposes only. GCT relied on roofline emission measurements previously performed for SO_2 and PM at other comparable smelters. The ratio of roofline SO_2 to PM emissions varies significantly from smelter to smelter, but the operations during the measurement campaigns at the other smelters are similar to the current operation at La Caridad. Therefore, a combination of the SO_2 to PM emission ratio from other comparable smelters were used to estimate the roofline PM emissions at La Caridad.

SULPHUR DIOXIDE EMISSIONS ASSESSMENT

Emissions testing

During a 10-day testing period, GCT performed continuous gas analyses (SO₂ concentration and temperature) for each roofline location as indicated in Figure 1 below. The different process areas are identified as follows:

- FSF building roofline (FB1, FB2, FB3)
- MTC and PSC no. 2 (FB4, CB1, CB2)
- PSCs no. 2, 3, and 4 (CB2, CB3, CB4)
- ARFs no. 1, 2 and 3 roofline (AB1, AB2, AB3)



Figure 1. La Caridad smelter roofline sampling locations map

A 12-m wide manifold was constructed using 9 mm stainless steel tubing for each sampling location, which included 4 extraction points. A pump was used to extract gas samples from the roof monovents through the manifold and direct a portion of the sampled gas to a Testo 350XL gas analyzer to measure SO_2 concentration and temperature. The Testo units were calibrated prior to shipment to site using a known sample gas to confirm measured concentration of each gas constituent. Three separate manifold/analyzer systems were set up to allow simultaneous and continuous measurements at three locations each day.

Roofline ventilation measurements (velocity and temperature) were made at each monovent daily as part of the building ventilation survey. The velocity and temperature measurements were used in conjunction with the monovent opening area to calculate the volumetric flow rate through the roof monitor for each measurement area. The calculated flow rate was then used with the logged SO_2 concentration data to calculate the SO_2 emission rate.

Aisle activities in the areas where the roofline testing was occurring were observed and logged. The logged activities included matte tapping from the furnaces, ladle movements, PSC secondary activities, ladle cleaning, and fume flow patterns and operating status of PSCs, ARFs, etc. Operator log sheets for the FSF, SCF, MTC, PSCs, and ARFs were obtained for the period when roofline emissions were measured.

Based on logged observations and the operator log sheets, the likely cause for each major roofline emission spike measured by the gas analyzers was identified. Using the continuous concentration measurements and the periodic velocity and temperature measurements, the average mass emissions rate (kg/h) during each major spike was calculated. Using the emissions rate, duration, and frequency of each activity spike, GCT estimated the daily average SO₂ emissions rate associated with specific aisle activities, such as matte charging to PSCs, slag return from PSCs to the SCFs, etc.

Volumetric flowrate and continuous SO_2 concentration measurements were taken in the SCFs fugitive emissions handling system stack, the Furukawa dryer stack, the steam dryer stack, and the ARFs no. 2 and 3 stacks (the ARF no. 1 was off-line).

Smelter building ventilation surveys were also completed. These surveys were used to estimate the overall building ventilation rate for consideration in emissions reduction analysis. Refer to the Smelter Building Ventilation Survey section for more details.

Roofline testing results

A summary of the SO₂ daily average emissions is presented in Table 1. It was found that the converter aisle area represents the largest contribution with 318 kg/h SO₂, followed by the MTC area with 155 kg/h SO₂. The FSF and its tapping area emissions contribute 68 kg/h SO₂, while the ARFs aisle contributes the least with an emission rate of 56 kg/h SO₂. Together, the total daily average smelter roofline emission rate was 596 kg/h SO₂.

Table 1. Roc	ofline SO ₂ da	aily average emi	issions summary	1
	Location	Flow Rate Nm ³ /h	SO ₂ Daily Ave	erage Emissions kg/h
		/	P P ····	8
FSF building roof monitors				
	FB1	460,000	6.86	9.0
	FB1	460,000	2.31	3.0
	FB1	460,000	8.97	11.7
	FB1	460,000	4.89	6.4
		FB1 average	5.76	7.5
	FB2	409,000	8.78	10.2
	FB2	409,000	6.91	8.1
	FB2	409,000	18.45	21.5
	FB2	409,000	12.24	14.3
		FB2 average	11.60	13.5

			,					
	Flow Rate		rage Emissions					
Location	Nm ³ /h	ppm	kg/h					
FSF building roof monitors (continued)								
FR2	460.000	36.20	17 5					
	460,000	25.23	47.5					
	400,000	22.10	12.2					
ГВЭ	460,000	55.10	45.5					
FB3	460,000	46.96	61.4					
	FB3 average	35.56	46.5					
FSF building roof mon	nitor total SO ₂		68					
MTC roof monitors								
FB4	486.000	35.69	49.5					
FB4	486,000	43.13	59.8					
FR4	486,000	56.67	78.6					
FR/	486,000	86.47	119.9					
	400,000	00.47	117.7					
	FB4 average	55.49	76.9					
CB1	227,000	129.5	83.7					
CB1	227,000	189.9	122.8					
CB1	227,000	58.4	37.8					
CB1	227,000	107.2	69.3					
	CB1 average	121.3	78.4					
MTC roof mor	nitor total SO ₂		155					
PSC s roof monitors								
CB2	203 000	87 1	50.3					
CB2	203,000	324.3	187.2					
CD2 CD2	203,000	324.3	107.2					
CB2	203,000	212.7	122.8					
CB2	203,000	196.0	113.2					
CB2	203,000	102.0	58.9					
CB2	203,000	157.6	91.0					
	CB2 average	179.9	103.9					
CB3	224,000	187.3	119.6					
CB3	224,000	95.5	61.0					
CB3	224,000	111.1	71.0					
	CB3 average	131.3	83.9					
CB4	238,000	279.3	189.8					
CB4	238.000	146.6	99.6					
CB4	238,000	147.1	100.0					
	CB4 average	191.0	129.8					
PSCs roof mor	nitor total SO_2		318					

	Location	Flow Rate Nm ³ /h	SO ₂ Daily Ave	erage Emissions kg/h	
ARFs aisle roof monitors					
	AB1	628,000	2.4	4.4	
	AB1	628,000	8.6	15.4	
	AB1	628,000	18.9	33.8	
		AB1 average	10.0	17.9	
	AB2	778,000	1.4	3.2	
	AB2	778,000	9.8	21.7	
	AB2	778,000	9.6	21.3	
		AB2 average	6.9	15.4	
	AB3	1,788,000	2.7	14.0	
	AB3	1,788,000	5.6	28.5	
	AB3	1,788,000	4.9	25.0	
		AB3 average	4.4	22.5	
AF	RFs roof mo	nitor total SO ₂		56	
Smelter roof total SO2 emissions596					

Table 1. Roofline SO₂ daily average emissions summary (continued)

Emissions associated with specific secondary activities were also evaluated. The magnitude, duration, and frequency of the SO₂ measured peaks were identified to quantify the amount of roofline SO₂ emitted from the secondary activities. Table 2 presents a summary of SO₂ emissions from the various secondary activities. The area with the highest total secondary activity roofline emission rate is the MTC aisle with a total secondary activity emission rate of 95.2 kg/h, followed by the PSC area with a total emissions rate of 52.3 kg/h. The FSF and SCF building experience a total emission rate of 15.3 kg/h while the ARF aisle has a total roofline emission rate of 1.8 kg/h from secondary activities. Together, the secondary activities from the four areas above result in a total roofline daily average emission rate of 165 kg/h SO₂.

Table 2. Summary of SO_2 roofline emissions from secondary activities								
	Instantaneous emission rate (kg/h)	Emissions per event (kg/event)	Events per day	Total em (kg/day)	issions (kg/h)			
FSF and SCFs building								
FSF matte tapping	59.4	15.9	$12^{Note \ I}$	191.1	8.0			
SCF1 slag return	58.0	2.5	6	15.2	0.6			
SCF2 slag return	280.3	9.3	12	111.2	4.6			
SCF1 matte tapping	17.6	4.1	8	32.5	1.4			
SCF2 matte tapping	10.0	1.3	7	9.0	0.4			
FSF slag tapping	1.5	1.3	6	7.9	0.3			
	s building total	367	15.3					

Note 1: represents matte taps that occur simultaneously

Tuble 2. Bullinary o	Instantaneous Emissions		Total em	issions	
	emission rate (kg/h)	per event (kg/event)	Events per day	(kg/day)	(kg/h)
MTC building					
MTC roll-in / roll-out	1375.4	70.7	70.7 4		11.8
MTC matte tapping	403.2	73.0	12	876.3	36.5
MTC matte ladle out of bay	59.8	4.6	12	54.8	2.3
MTC slag tapping	238.1	152.8	7	1,069.8	44.6
		MTC	C building total	2,284	95.2
PSCs aisle building					
PSC roll-in / roll-out	774.7	7.7	69	534.5	22.3
Oxide slag addition	407.1	8.1	12	97.7	4.1
Charge	541.6	8.7	8.7 26		9.5
Boat/scrap	459.9	14.9	14.9 18		11.2
Blister pouring	190.2	2.7	21	57.7	2.4
Skimming	601.7	4.7	4.7 15		2.9
		PSCs aisle	PSCs aisle building total		52.3
ARFs aisle building					
Charging	48.7	0.8	21	16.8	0.7
Boat/scrap	30.1	0.5	4	2.0	0.1
Skimming	82.9	6.2	4	24.9	1.0
		ARFs aisle	e building total	43.6	1.8
	,	Total secondary	SO ₂ emissions	3,950	165

Table 2. Summary of SO₂ roofline emissions from secondary activities (continued)

Using the total emissions measured at the roofline and the emissions due to secondary activities, the background emissions can be estimated. The background emissions generally consist of FSF and MTC fugitive emissions, PSC blowing fugitive emissions, and emissions released from ladle movements (e.g., recently emptied ladles). Table 3 presents the roofline SO_2 emissions breakdown by smelter area.

Table 3. Roofline SO ₂ emissions breakdown										
	Smelt	ter total	FSF b	ouilding	MT	C area	PSCs	s aisle	ARF	⁷ aisle
Emission Type	kg/h	%	kg/h	%	kg/h	%	kg/h	%	kg/h	%
Secondary	165	28%	15	23%	95	61%	52	16%	2	3%
Background	432	72%	52	77%	60	39%	265	84%	54	97%
Total emissions	596	100%	68	100%	155	100%	318	100%	56	100%

Overall sulfur fixation performance

The total SO₂ emission rate from the smelter is 1,674 kg/h (13,388 t/y), with 777 kg/h from the various stacks and 896 kg/h from roofline fugitive emissions. The quantification of roofline fugitive emissions includes an estimate of 300 kg/h SO₂ as emissions escaping through the building sidewalls. At an average FSF concentrate feed rate of 80 t/h (35.15 wt% S and 21.83 wt% Cu) and an average MTC feed rate of 55 t/h (35.15 wt% S and 21.83 wt% Cu), total sulfur emissions are estimated to be 56.8 kg SO₂/tonne Cu in concentrate, with an overall sulfur fixation of approximately 98.2%.

PARTICULATE MATTER EMISSIONS ASSESSMENT

Table 4 summarizes the total smelter stack and roofline SO_2 and PM emissions estimates based on GCT's measurements, stack emissions data provided by La Caridad, and the estimated roofline PM emissions (using the SO_2 to PM ratios previously observed in other comparable copper smelters; refer to the Evaluation Approach section in this paper).

Table 4. Smelter SO ₂ and PM emissions							
		S	O_2	PM			
		kg/h	t/y	kg/h	t/y		
	Acid plant 1 tail gas	494.4	3,955	0.0	0.0		
	Acid plant 2 tail gas	236.1	1,889	0.0	0.0		
	Fugitives baghouse ²	33.0	264	0.8	6.4		
	Flash dryer ²	8.4	67	1.6	12.8		
Stacks	ARF stacks ³	5.2	42	24.8	198.4		
	Steam dryer ²	0.2	1.3	2.5	19.8		
	PSC secondary hoods ⁴	-	-	-	-		
	Stacks total	777	6,219	29.7	237		
	PSCs aisle	318	2,541	12.1	55.8		
	MTC	155	1,242	5.9	27.3		
	FSF / SCFs and tapping	68	54	4.1	32.4		
Roof ¹	ARFs aisle	56	446	8.2	47.0		
	Sidewall emissions ⁵	300	2,400	11.5	92		
	Roofline total	896	7,170	41.8	335		
	Smelter total	1,674	13,388	71.5	572		

Notes:

1 - Roofline PM emissions estimated based on SO₂/PM ratio measured at other smelters

2 - Stack PM emissions as measured by La Caridad

3 - PM emissions rate estimate scaled from data collected at other smelters

4 – Did not operate during site visit

5 – GCT's estimate

As Table 4 shows, the total PM emissions rate from the smelter is estimated at 71.5 kg/h (572 t/y), with 29.7 kg/h from the stacks and 41.8 kg/h from roofline fugitive emissions.

SMELTER BUILDING VENTILATION SURVEY

Ventilation measurements (velocity and temperature) were undertaken at various openings around the smelter, including the roofline monovents. The velocity and temperature measurements were used in conjunction with the opening areas to calculate the volumetric flowrate through each measurement area. The ventilation survey presents magnitude and direction of the flowrate to determine whether or not air entering the smelter can cause cross-drafts and disturb air flow patterns. Figure 2 presents a ventilation survey diagram which summarizes the flowrates measured at the various smelter openings. The diagram shows that east-towest prevalent winds result in ambient air flowing in and out of the building through the east and west sides, respectively.



Figure 2. Ventilation survey diagram

EMISSIONS ABATEMENT IMPROVEMENT OPPORTUNITIES

Based on the SO_2 and PM emission assessments, different areas of opportunity were identified as of highest priority to reduce SO_2 and PM emissions from the smelter. These areas of opportunity are summarized in this section.

PSC process gas capture improvements

The PSC area represented the highest priority area for improvement. Each PSC has a water-cooled primary hood to capture process gases from blowing. The primary hoods have significant gaps between the hood and the converter vessel that allow a high rate of ambient air infiltration into the hood. As a result, the process gas system cannot fully capture all of the process gases from the converters, and higher fugitive emissions are generated and released into the aisle. It was identified that approximately 800 kg/h of SO₂ escaped the primary hoods and was not captured by the secondary hoods. The secondary hood system was off-line, which resulted in fugitive emissions reporting directly to the converter roofline.

During GCT's assessment, the PSCs were also observed to experience high levels of fugitive emissions due to blowing during PSC roll-in and roll-out activities. Blowing controls during roll-in and roll-out can be optimized to reduce the fugitive emissions generated during this activity.

The primary process gas handling system captures and conditions the process gas from the FSF, the MTC, and the PSCs, and sends it to the two acid plants for further cleaning and sulfur recovery. The distribution of draught from the five process vessels to the two acid plants is complex and the current control and operation logic is insufficient. An effective control strategy can ensure safe and reliable operation while optimizing exhaust distribution in order to maximize capture performance and minimize fugitive emissions from the process vessels.

The current process gas handling system consists of two long parallel ducts that combine at a mixing duct immediately upstream of the two acid plants. The PSCs gas combines with the FSF off-gas and enters the mixing duct through the south end, while the MTC off-gas enters through the east side of the mixing duct. The current mixing duct arrangement does not provide a good mixing configuration, which leads to unequal SO_2 distribution to the two acid plants. In addition, the two long ducts handle different process gases, which results in significant thermal cycling. The thermal cycling and age of the ducts allows for significant air infiltration. Due to this reason, it was recommended that the process gas handling ductwork be modified to have a single common duct.

By implementing the process gas handling system modifications, the smelter fugitive SO_2 emissions would be reduced by 563 kg/h (4,500 t/y), while the PM emissions would be reduced by approximately 27 kg/h (219 t/y).

ARFs new process gas handling system

Each ARF currently has an end-wall off-gas port with a combustion chamber which exhausts ARF off-gas to atmosphere via a stack through the ARFs building roof. The current off-gas configuration cannot fully draught all of the generated off-gas, and much of it escapes through the uncovered charging mouth. Even though SO_2 generation at the ARFs is much lower than in the other vessels, it is important to capture this gas in order to reduce the PM and metals emissions at the ARF roofline.

GCT recommended the installation of furnace mouth covers and a new baghouse-based off-gas cleaning system to capture and treat the ARF off-gas. GCT completed basic and detailed engineering for this new off-gas handling system consisting of three extraction hoods, one common ductwork, one common evaporative cooler, a dedicated baghouse, I.D. fan and stack. During 2016 and 2017, in preparation to implement the new ARFs gas handling system, the ARFs no.1 and no.2 were replaced by new and longer

ARFs. The new ARFs length was increased by 2 meters to enable the introduction of a new off-gas port separate from the charge mouth. The ARFs gas handling system project is in procurement phase with commissioning estimated during 2021.

MTC and PSCs secondary off-gas handling system improvements

GCT recommended the installation of a secondary hood for the MTC and tying it into the PSC secondary gas system, while increasing the processing capacity of the system. As witnessed during the ventilation surveys and aisle observations, cross-drafts inside the converter aisle cause the fugitive emissions escaping the converter primary hoods and fugitive emissions from secondary activities to drift across the aisle either towards the MTC and FSF area or the ARFs area. It is expected that most of the emissions measured at the ARFs roofline are from the PSC aisle.

If secondary hood capture performance can be increased to 90% and SO₂ dry scrubbing performance increased to 60%, the MTC area, PSC area, and ARF area SO₂ emissions should see a reduction of approximately 152 kg/h (1,214 t/y) while the smelter PM emissions would be reduced by approximately 10 kg/h (77 t/y). These capture and scrubbing efficiencies have been demonstrated at other comparable copper smelters.

GCT was tasked with the development of basic and detailed engineering of a new secondary hood and ventilation systems for slag tapping and white metal tapping from the MTC while tying into the existing PSC secondary off-gas handling system. The project is currently in construction phase with expected start-up during 2020.

Secondary areas of opportunity

Other secondary priority areas of opportunity were identified and proposed to be addressed upon completion of the higher priority improvements. These secondary priority areas are:

- Improvements to FSF area:
- Tapping ventilation
- Fugitive emissions baghouse hydrated lime for SO₂ scrubbing
- New slag return ventilation hoods over SCFs no. 1 and 2
- Improvements to MTC tapping ventilation area via the installation of new MTC tapping hoods
- Evaluate installation of new water-cooled primary hoods for PSCs
- Install new PSC area tertiary baghouse system to capture fugitive emissions
- Install acid plant tail gas scrubbers

WAY FORWARD

As a result of GCT's assessment and subsequent work, the La Caridad smelter have made significant capital investments to implement the emissions abatement projects. Once the changes to the off-gas and fugitives handling systems (PSCs, MTC, and ARFs) are fully implemented, a new inventory of SO_2 emissions will be undertaken to confirm or re-assess the next areas of improvement opportunities which must be addressed in the future.

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